Photodegradation of environmental pollutants using perylene adsorbed on silica gel as a visible-light photocatalyst

Hiroshi Moriwaki [a,b,*], Yasutaka Akaishi [a], Michiya Akamine [a], Hisanao Usami [c]

[a] Shinshu University, Faculty of Textile Science and Technology, Division of Applied Biology, 3-15-1, Tokida, Ueda 386-8567, Japan
[b] Shinshu University, Division of Instrumental Analysis (Ueda branch), Research Center for Human and Environmental Sciences, 3-15-1, Tokida, Ueda 386-8567, Japan
[c] Shinshu University, Faculty of Textile Science and Technology, Division of Chemistry and Materials, 3-15-1, Tokida, Ueda 386-8567, Japan

ARTICLE INFO

ABSTRACT

Decomposition of several environmental pollutants in water using perylene adsorbed on silica gel (Pe/SiO_2 powder) as a photocatalyst under the visible-light irradiation have been studied. The Pe/SiO_2 powder was prepared by mixing a toluene solution of the perylene with silica gel followed by evaporating the toluene. Irradiation by visible light (>420 nm) of the methyl orange aqueous solution with the Pe/SiO_2 powder in the presence of ascorbic acid resulted in the decomposition of the methyl orange. The rate of decrease of the methyl orange reached 99% by visible light irradiation for 20 min. The reaction also occurred by the irradiation of sunlight. In addition, the irradiation of visible light also led to the decomposition of imidacloprid using Pe/SiO_2 in the presence of ascorbic acid. Furthermore, irradiation by visible light (>420 nm) of a pentachlorophenol aqueous solution with the Pe/SiO_2 powder resulted in the decomposition of the pentachlorophenol. The possible mechanisms of these reactions are discussed.

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1. Introduction

Applications of solar power to environmental water clean-up technology have received much attention because the drain of fossil energy resources is a concern. Since the 1970s, various photocatalysts have been developed, and applied to environmental purification. Titanium oxide (TiO_2), in particular, has been widely used as a photocatalyst to decompose many kinds of organic pollutants [1–6]. However, TiO_2 is not excited by visible light irradiation, and ultraviolet radiation is required to use TiO_2 as a photocatalyst. The ultraviolet portion in the solar spectrum is very small (~6%), while visible light occupies 52% of the spectrum [7]. Therefore, the development of materials, which shows a catalytic activity under visible light, are expected. Recently, the modifications of TiO_2 for the utilization of visible light, such as doping, dye sensitization, and coupling semiconductors, have been extensively studied [8].

In a previous study, we reported that the irradiation of visible light led to the decomposition of methyl orange using C_{60} fullerene adsorbed on silica gel (C_{60}/SiO_2) as a photocatalyst in the presence of ascorbic acid [9]. Irradiation by visible light or sunlight of the methyl orange aqueous solution (10 mL, 25 μM) for 30 min in the presence of C_{60}/SiO_2 (20 mg) and ascorbic acid (0.5 mM) resulted in the decomposition of the methyl orange of over 90%. Furthermore, continuous photodecomposition of the methyl orange using the C_{60}/SiO_2 packed column was achieved.

The C_{60}/SiO_2 can be used as a photocatalyst for the degradation of azo dyes, such as methyl orange and methyl red. However, the decomposition of other chemicals using the C_{60}/SiO_2 as a photocatalyst could not be observed. The results would depend on the low reduction ability of the C_{60}/SiO_2. The excited C_{60}/SiO_2 accepts an electron from ascorbic acid during of the photoreaction, and forms a radical anion of C_{60}. The electron transfer from the radical anion of C_{60} to the compounds other than the azo dyes would not efficiently occur because of the low reduction potential of the C_{60} fullerene (-0.42 V vs. SCE in benzonitrile) [10]. In addition, C_{60} fullerene is very expensive, which makes it difficult to use C_{60} for environmental clean-up technology.

In this report, the photoreactions of environmental pollutants using perylene adsorbed on silica gel (Pe/SiO_2) as a visible light active catalyst are described. The reductive potential of perylene (-2.0 V vs. SCE in CH_3CN) is more negative than that of C_{60} [11]. Therefore, it is expected that the non-metal material could be

* Corresponding author at: Shinshu University, Faculty of Textile Science and Technology, Division of Applied Biology, 3-15-1, Tokida, Ueda 386-8567, Japan.
E-mail address: moriwaki@shinshu-u.ac.jp (H. Moriwaki).

applied to the decomposition of various environmental organic pollutants. SiO_2 was used as a support material in order to disperse perylene in an aqueous solution.

Perylene has an absorption at visible light region. The carcinogenicity of perylene is much lower than those of the other polycyclic aromatic hydrocarbons, such as benzo[a]pyrene and benzo[ghi]perylene [12]. Furthermore, the water solubility of perylene is very low.

Environmental organic pollutants, methyl orange, imidacloprid, and the pentachlorophenol sodium salt, were selected as substrates for the photoreaction using Pe/SiO_2 as the photocatalyst. Methyl orange is an anionic azo dye, and often used as a model compound for photoreactions. This dye has a mutagenic activity [13]. Imidacloprid is a neonicotinide pesticide, which is possibly the be causative substance for the bee colony collapse disorder [14]. Pentachlorophenol was used as a pesticide, but its toxicity, such as its harmful effects on the liver, kidneys, and nervous system, is so high that the preparation and use of this compound have been restricted in many countries [15]. Pentachlorophenol and its salts and esters were recently listed as new POPs (persistent organic pollutants) under the Stockholm Convention in 2015 [16]. These pollutants are highly-polar compounds and water soluble, and it has been a concern that they widely diffuse in the water environment and exert harmful effects on living creatures [17].

2. Experimental

2.1. Materials and chemicals

Perylene, methyl orange, methyl red, imidacloprid, pentachlorophenol sodium salt, ascorbic acid, acetonitrile (HPLC grade), methanol (HPLC grade), chloranil, 2-propanol, acetic acid, ammonium acetate, toluene, triethylamine, chloranil, sodium hydroxide and SiO_2 for column chromatography (particle diameter: 20–40 μm) were obtained from Wako Pure Chemical Industries (Osaka, Japan). All reagents were used without further purification.

Pure water was prepared by an automatic water distillation apparatus (MQ academic A10, Millipore, Billerica, MA, USA). The synthesis of 2,5,6-trichloro-3-hydroxy-1,4-benzoquinone was carried out by a procedure reported in Reference [18].

2.2. Preparation of Pe/SiO_2

The preparation method of Pe/SiO_2 was similar to that of C_{60}/SiO_2 described in our previous report [9]. The SiO_2 powder (1.0 g) was added to the perylene toluene solution (20 mL, 1000 μg mL^{-1}), then the toluene was removed by a rotary evaporator. The obtained pale yellow powder was freeze-dried. The powder was next washed with distilled water in order to remove the perylene, which is not tightly adsorbed on the silica gel. The Pe/SiO_2 powder was mixed with distilled water (40 mL) for 30 min by a stirrer bar followed by filtration and drying.

The quantity of perylene adsorbed on the Pe/SiO_2 powder was determined. The powder (20 mg) was initially extracted by acetonitrile (10 mL). The concentration of perylene in the acetonitrile-extracted solution was determined by HPLC. A liquid chromatography system consisting of a Shimadzu (Kyoto, Japan) LC-20AD constant volume pump and UV absorbance detector (SPD-20A UV-vis, Shimadzu, 254 nm) was used. An L-column ODS (Chemicals Evaluation and Research Institute, Tokyo, Japan: 5 μm particle size, 2.1mm × 150mmi.d.) was used for the LC separation of the perylene. The HPLC separation was carried out at 40 °C. The flow rate was 0.20 mL min^{-1}, and the injection volume was 10 μL. As a result, 3.5 mg of perylene was adsorbed onto 1.0 g of the SiO_2 powder. When the powder (50 mg) was stirred in distilled water (10 mL)

for 1 h, there was no perylene separated from the powder onto the liquid. The filtrate of the solution was extracted by toluene, and the concentration of perylene dissolved in the aqueous solution was determined. The perylene concentration was 0.042 mg L^{-1}. This result indicated that the dissolution of perylene from Pe/SiO_2 occurs by mixing in aqueous solution. However, the desorption (in percent) of perylene from Pe/SiO_2 was below 0.2% of the adsorbed perylene on the powder. The Pe/SiO_2 powder was characterized by FT-IR (FT/IR-6700FV, JASCO, Tokyo, Japan). The material was kept in the dark at room temperature, and used within a few weeks of its production. The Pe/SiO_2 powder was stored under a nitrogen atmosphere.

2.3. Photoreactions of environmental pollutants using Pe/SiO_2

The general procedure of the photoreactions of environmental pollutants using Pe/SiO_2 is represented by the reaction of methyl orange. The irradiation of a methyl orange aqueous solution (50 μM, 10 mL) with the Pe/SiO_2 powder (50 mg) in the presence of ascorbic acid (1.0 mM) was carried out using a xenon lamp (300 W cm^{-2}, RSX-500 and LHX-500, Koken Kogyo, Saitama, Japan) through a filter (>420 nm, L42, Hoya, Tokyo, Japan). The pH value of the solution was 3.5–3.7. The Pe/SiO_2 powder was dispersed in the reaction liquid by a stirrer bar during the irradiation. The temperature of the reaction liquid was maintained at 20 °C by a constant-temperature bath.

The reuse of the Pe/SiO_2 powder was studied. The photodecomposition of methyl orange using the same Pe/SiO_2 powder was repeated. The reaction liquid after the photoreaction was centrifuged (3000 rpm, 3 min), and the supernatant was removed from the tube. The residue was mixed with the methyl orange aqueous solution (25 μM, 10 mL) containing ascorbic acid (1 mM), and irradiated again. The UV spectrum of the obtained supernatant was measured by a UV absorption spectrometer (V-630, JASCO Corporation, Tokyo, Japan). The methyl orange concentration was calculated by the absorbance at 500 nm. After filtration through filter paper (No. 5A, Advantec,Tokyo, Japan), the obtained solution was analyzed by electrospray ionization/mass spectrometry (ESI/MS) in both the positive and negative ion modes for the detection and identification of the products by the photoreactions and liquid chromatography (LC)/MS for their determination. The photoreactions for methyl orange and imidacloprid by sunlight were studied (Ueda City, Nagano, Japan). The solar radiation was monitored for 5 min by a photometer (LM-230, As One, Osaka, Japan), and the solar radiation in this study was approximately 200 W m^{-2}.

2.4. Photoreactions of methyl orange by the continuous flow system

The Pe/SiO_2 column was prepared by packing 700 mg of Pe/SiO_2 powder into a Pasteur pipette (7 mm inner diameter)stuffed with cotton. The length of the column was 5.5 cm. The methyl orange (25 μM) aqueous solution containing ascorbic acid (2.0 mM) was pumped through the Pe/SiO_2 column by a microtube pump (EYELA, Tokyo, Japan) at 0.40 mL min^{-1}. The solution was held in the column for 180 s. The column was irradiated by a xenon lamp or sunlight. Fractions of the solution through the column were sampled and analyzed by UV absorption, ESI/MS and LC/MS.

2.5. Analysis of the degradation of pollutants by the photoreactions

The obtained sample solutions were filtered using a cellulose acetate filter (pore diameter: 0.45 μm), and analyzed by ESI/MS
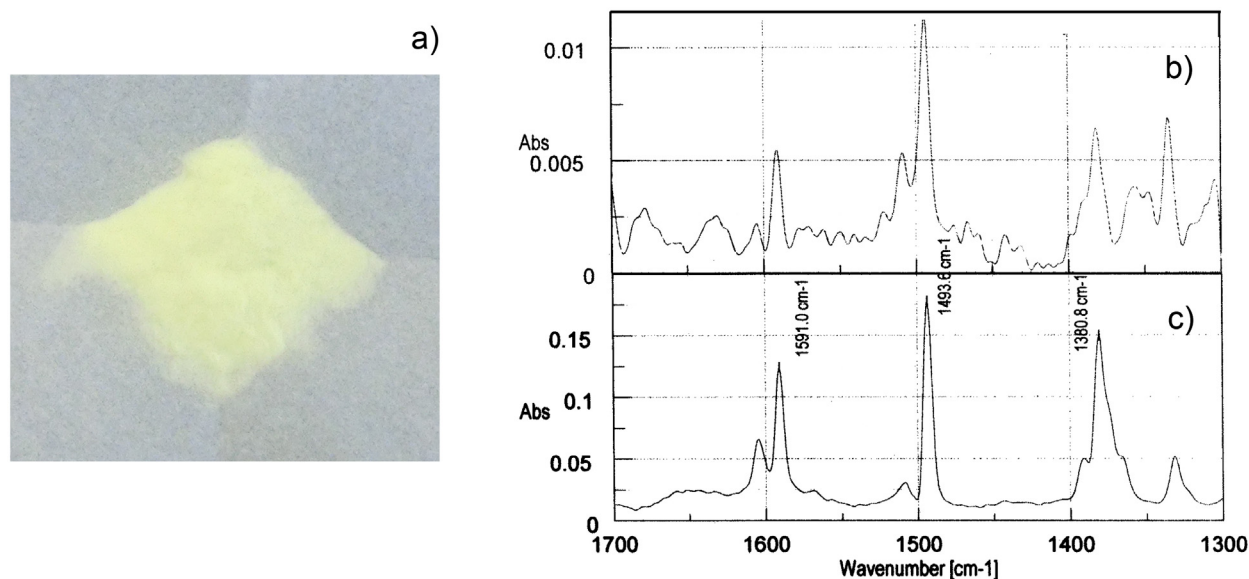
Fig. 1. (a) Photograph of Pe/SiO$_2$ powder. (b) The difference spectrum between the diffuse reflectance infrared vibrational spectrum of Pe/SiO$_2$ and that of SiO$_2$. (c) The diffuse reflectance infrared vibrational spectrum of the single-crystal perylene.

in the positive and negative ion modes (LC/MS 2010A, Shimadzu, Kyoto, Japan). The ESI/MS conditions were as follows: scan range, m/z 50–500; heat block temperature, 200 °C; interface voltage, 4.5 kV; CDL voltage, 15 V; injection volume, 10 μL; and the flow rate, 0.20 mL min^{-1}.

The filtered reaction solutions were also analyzed by LC/MS. The reaction substrate and products were separated by a TSK gel ODS 100Z (Tosoh, Tokyo, Japan: 5 μm particle size, 2.0 × 150 mm i.d.). For the analysis of the products of the methyl orange and imidacloprid, the HPLC conditions were as follows: column temperature, 40 °C; flow rate, 0.20 mL min^{-1}. The mobile phase was composed of solution A (0.1% acetic acid aqueous solution) and solvent B (methanol). The gradient conditions were as follows: 0–5 min, hold at 10% B; 5–10 min, a linear increase from 10 to 90% B; 10–20 min, hold at 90% B. The LC/MS acquisition was performed in the selected ion monitoring (SIM) mode at m/z 137 for N,N-dimethyl-p-phenylenediamine, m/z 172 for sulfanilic acid, and m/z 256 for imidacloprid, respectively. The detection limits (S/N 3) were 0.04, 0.005, and 0.002 μM for N,N-dimethyl-p-phenylenediamine, sulfanilic acid, and imidacloprid.

For analysis of the PCP and the products, the HPLC conditions were as follows: column temperature, 40 °C; flow rate, 0.20 mL min^{-1}. The mobile phase was composed of solution A (0.3% acetic acid aqueous solution) and solvent B (methanol). The gradient conditions were as follows: 0–5 min, hold at 10% B; 5–15 min, a linear increase from 10 to 99% B; 15–25 min, hold at 99% B. The LC/MS acquisition was performed in the negative ion mode and the selected ion monitoring (SIM) mode at m/z 265 for pentachlorophenol (PCP), and m/z 225 for 2,5,6-trichloro-3-hydroxy-1,4-benzoquinone (TCHB). The detection limits (S/N 3) were 0.0002 and 0.005 μM for PCP and TCHB, respectively.

In the case of the photoreaction of imidacloprid and PCP, the concentrations of nitrate and chloride in the reaction solution were analyzed by ion chromatography (ICS-1600, Dionex, USA, Massachusetts). The separation of the negative ions was achieved using Dionex Ion Pac AS-12A (Thermo Scientific, USA, Massachusetts, 4.0 × 200 mm). The separation conditions were as follows: column temperature, 30 °C; flow rate, 1.20 mL min^{-1}. The mobile phase was a Na$_2$CO$_3$ (0.0027 mol L^{-1}) and NaHCO$_3$ (0.00030 mol L^{-1}) aqueous solution.

3. Results and discussion

3.1. Characterization of Pe/SiO$_2$ powder

The Pe/SiO$_2$ powder was yellow (Fig. 1a), and has an absorption band in the visible light region (400–500 nm). The difference spectrum between the diffuse reflectance infrared vibrational spectrum of Pe/SiO$_2$ and that of SiO$_2$ was similar to that of the single-crystal perylene (Fig. 1b and c). On the other hand, significant particles or crystals were not observed on the surface of the Pe/SiO$_2$ by the SEM or TEM measurements. These results indicated that perylene in the powder very thinly distributes onto the surface of SiO$_2$. In addition, the zeta potentials of Pe/SiO$_2$ and SiO$_2$ were −32 and −3.3 mV at pH 4, respectively.

3.2. Photoreaction of methyl orange in the presence of Pe/SiO$_2$ powder and ascorbic acid

The irradiation by visible light (>420 nm) of the methyl orange aqueous solution in the presence of the Pe/SiO$_2$ powder and ascorbic acid resulted in the decolorization of the solution (Fig. S1). Significant changes in the pH of the solution were not observed before and after the photoreaction (pH 3.5–3.8). Methyl orange was slightly removed by mixing with the Pe/SiO$_2$ powder in the dark. However, no peaks corresponding to the products of the methyl orange were observed by ESI/MS. This result indicates that methyl orange adsorbs onto the surface of the Pe/SiO$_2$. Methyl orange was not decomposed by the visible light irradiation without Pe/SiO$_2$. The photoreaction of methyl orange with Pe/SiO$_2$ in the absence of ascorbic acid also did not occur. These results are summarized in Table 1.

The variation in the rate of decrease (%) of the methyl orange versus the ascorbic acid concentration are shown in Fig. S2. The rate of decrease of methyl orange was over 95% under visible light irradiation for 20 min when the ascorbic acid concentration was greater or equal to 1.0 mM. The effects of the amounts of the Pe/SiO$_2$ powder on the rate of decrease (%) of the methyl orange was also investigated (Fig. S3). The rate of decrease of the methyl orange increased as the amount of the Pe/SiO$_2$ powder was increased from 2.5 to 50 mg 10 mL^{-1}. For a Pe/SiO$_2$ amount of 100 mg 10 mL^{-1}, the

Table 1
Photoreaction of methyl orange using Pe/SiO$_2$ as a photocatalyst[a].

Entry	Additives	Atmosphere	Light	Irradiation time (min)	Rate of decrease (%)
1	Pe/SiO$_2$	Air	Visible light (>420 nm)	20	15
2	Ascorbic acid (AA)	Air	Visible light (>420 nm)	20	12
3	None	Air	Visible light (>420 nm)	20	4.7
4	Pe/SiO$_2$	Air	Dark	20	14
5	Pe/SiO$_2$ + AA	Air	Dark	20	14
6	Pe/SiO$_2$ + AA	Air	Visible light (>420 nm)	10	47
7	Pe/SiO$_2$ + AA	Air	Visible light (>420 nm)	20	99
8	Pe/SiO$_2$ + AA	N$_2$	Visible light (>420 nm)	10	35
9	Pe/SiO$_2$ + AA	N$_2$	Visible light (>420 nm)	20	84
10	Pe/SiO$_2$ + AA + 2-propanol[b]	Air	Visible light (>420 nm)	10	39
11	Pe/SiO$_2$ + AA + 2-propanol	Air	Visible light (>420 nm)	20	93
12	Pe/SiO$_2$ + AA	Air	Sunlight	10	66
13	Pe/SiO$_2$ + AA	Air	Sunlight	20	88

[a] The initial concentrations of methyl orange and ascorbic acid were 50 μM and 1.0 mM, respectively. The quantity of Pe/SiO$_2$ was 50 mg/10 mL.

[b] The concentration of 2-propanol was 0.1 M.

rate of decrease of the methyl orange slightly decreased compared to that at 50 mg 10 mL^{-1}. Based on these results, the concentrations of ascorbic acid and the Pe/SiO$_2$ powder were set at 1.0 mM and 50 mg 10 mL^{-1}, respectively.

The plot of C_t/C_0 of the methyl orange versus time shows an approximate linearity (Fig. **S4**), where C_0 is the initial concentration of methyl orange and C_t is the concentration after the irradiation for t min. On the other hand, the plot of $-\ln C_t/C_0$ versus time did not show a linearity. This result indicated that the photoreaction did not fit a first-order kinetic model. The adsorption of methyl orange onto Pe/SiO$_2$ would affect the photoreaction of methyl orange with Pe/SiO$_2$ in the presence of ascorbic acid (Table 1, entry 5). After the photodecomposition of methyl orange at the adsorption site of Pe/SiO$_2$, other methyl orange molecules would then adsorb at the site and decompose.

The products of the photoreaction were determined to be N,N-dimethyl-p-phenylenediamine and sulfanilic acid by ESI/MS (Fig. S5) and LC/MS measurements. The retention times of these products in the LC/MS measurements were in agreement with those of the standard samples of N,N-dimethyl-p-phenylenediamine and sulfanilic acid. These products are similar to those of the photoreaction of methyl orange with C$_{60}$/SiO$_2$ in the presence of ascorbic acid [9]. The yields of N,N-dimethyl-p-phenylenediamine and sulfanilic acid were 55% and 63%, when the methyl orange aqueous solution (50 μM) with the Pe/SiO$_2$ powder in the presence of ascorbic acid (1.0 mM) was irradiated for 20 min (the conversion of methyl orange; 99%). The yields of the products were low compared to the conversion of methyl orange. This result indicated that there are several products, which were not detected by ESI/MS or the N,N-dimethyl-p-phenylenediamine and sulfanilic acid underwent further reactions. The formations of NO$_2^-$, NO$_3^-$, and SO$_4^{2-}$ in the filtered reaction solution were not observed.

Irradiation by visible light of the methyl red aqueous solution with the Pe/SiO$_2$ powder in the presence of ascorbic acid also resulted in the decolorization of the solution due to the decomposition of methyl red. Methyl red was decomposed by the visible light irradiation in the presence of C$_{60}$/SiO$_2$ and ascorbic acid [9].

The irradiation of sunlight also led to the decomposition of methyl orange using Pe/SiO$_2$ in the presence of ascorbic acid. The rate of decrease (%) of the methyl orange was 88% by the sunlight irradiation for 20 min (Table 1, entry 13). The products of the photoreaction were the same as those by the photoreaction using visible light.

The possible mechanism of the photoreaction of methyl orange in the presence of Pe/SiO$_2$ and ascorbic acid should be similar to that in the presence of C$_{60}$/SiO$_2$ and ascorbic acid. The photoreaction mechanism can be visualized as in Fig. S6. Thus, the electron transfer from the excited perylene to the protonated methyl orange

(quinoid structure) causes the bond cleavage of methyl orange to generate the products, N,N-dimethyl-p-phenylenediamine and sulfanilic acid. It was reported that the reduction level of perylene was −2.0 V (vs SCE, solvent: acetonitrile) and E$_s$ (^{1}Pe) was 2.85 eV, and the reduction potential of methyl orange (at pH 4) was −0.24 V (vs SCE) [19]. These reduction levels suggest that the electron transfer from the excited perylene to the quinoid structure of methyl orange should be spontaneous. Ascorbic acid will give an electron to the radical cation of perylene. The electron transfer is also feasible based on the oxidation potential of ascorbic acid (−0.117 V vs SCE) [20] and the oxidative potential of perylene (0.85 V vs SCE, solvent: acetonitrile) [11].

The rate of decrease (%) of methyl orange slightly decreased by the removal of oxygen (Table 1, entries 6 and 8 or entries 7 and 9). This result indicated that methyl orange slightly decomposes via the formation of the superoxide anion radical by electron transfer between the perylene radical anion and oxygen. The addition of 2-propanol decreased the rate of decrease (%) of methyl orange (Table 1, entries 6, 7, 10, and 11). The oxidation potential of 2-propanol was 2.88 V (vs SCE) [21], and the compound would not behave as an electron donor (Fig. S6). It is well known that 2-propanol scavenges radicals [22]. These results also indicated that the formation of the superoxide anion radical was relevant to the photodecomposition of methyl orange [23]. The probability of the intersystem crossing of perylene is low (ϕ_{ST}: 0.0088) [11]. Therefore, the influence of the $^1O_2$ formed by the energy transfer from the excited perylene to $^3O_2$ would slightly affect the photoreaction of methyl orange with Pe/SiO$_2$.

Methyl orange was not decomposed by the visible light irradiation (20 min) of a methyl orange aqueous solution (pH 4 adjusted by HCl) containing Pe/SiO$_2$ in the absence of ascorbic acid. This result indicates that the electron transfer between the excited Pe/SiO$_2$ and the protonated methyl orange did not occur without ascorbic acid because of the quenching of the excited perylene to the ground state.

In order to observe the reuse of the Pe/SiO$_2$ powder, the same Pe/SiO$_2$ powder was repeatedly used for the photodecomposition of methyl orange in water (Fig. S7). The rates of decrease (%) of the methyl orange were over 98% and did not significantly change throughout the photoreaction cycles (1–5 times). This result suggested that the Pe/SiO$_2$ powder can be repeatedly used as a visible-light photocatalyst to decompose methyl orange in water.

Next, the Pe/SiO$_2$ powder was applied to a continuous flow system for the photodecomposition of methyl orange. Fig. S8 is a schematic of the continuous flow system for the photodecomposition of methyl orange by the Pe/SiO$_2$ powder. As a result, the continuous color variation from orange to yellow was observed (Fig. 2). The methyl orange was decomposed in the Pe/SiO$_2$ col-
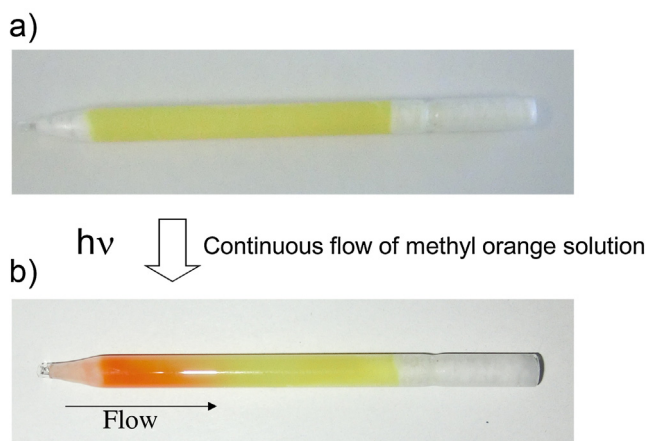
a)

hν ⬇ Continuous flow of methyl orange solution

b)

Flow →

Fig. 2. (a) The photograph of the Pe/SiO$_2$ column before the flow of the methyl orange aqueous solution. (b) The photograph of the Pe/SiO$_2$ column after the flow of the methyl orange aqueous solution and the irradiation of visible light for 1 h. The initial concentrations of methyl orange and ascorbic acid were 25 μM and 2.0 mM, respectively.

Fig. 3. The plots of C_t/C_0 of imidacloprid vs. irradiation time.

umn, and the rate of decomposition should increase with passage through the column. The color in the column was determined by the mixture of the color of methyl orange and that of the Pe/SiO$_2$ powder. Therefore, the color in the column was changed from orange to yellow with the flux of the reaction solution. The rate of decrease by the continuous reaction was over 98% for one hour. The products of the continuous reaction were N,N-dimethyl-p-phenylenediamine and sulfanilic acid similar to those of the batch reaction. The decomposition of methyl orange through the column did not occur in the dark or in the absence of ascorbic acid in the reaction solution.

The sunlight irradiation also led to the decomposition of methyl orange using Pe/SiO$_2$ in the presence of ascorbic acid. The rate of decrease of the methyl orange was over 85% for one hour. This result indicated that the Pe/SiO$_2$ can be applied to water clean-up technology using natural energy.

3.3. Photoreaction of imidacloprid in the presence of Pe/SiO$_2$ powder and ascorbic acid

The use of Pe/SiO$_2$ as a visible light responsive photocatalyst for the decomposition of imidacloprid was studied. The decomposition of imidacloprid after the visible light irradiation in the presence of the Pe/SiO$_2$ powder and ascorbic acid for 60 min was confirmed by measuring the filtered reaction solution by LC/MS. The rate of decrease was 99% by the visible light irradiation for one hour. The photoreaction did not occur in the dark. In addition, imidacloprid was not decomposed by the visible light irradiation of its aqueous solution in the absence of Pe/SiO$_2$ and/or ascorbic acid for one hour. The results are summarized in Table 2. Imidacloprid was
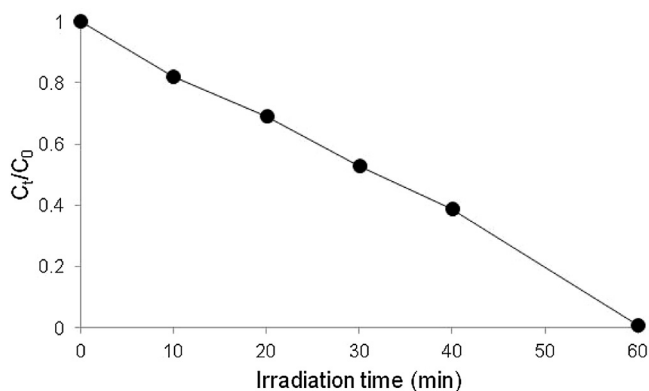
not decomposed by the visible light irradiation in the presence of C$_{60}$/SiO$_2$ and ascorbic acid. This result suggests that Pe/SiO$_2$ shows different catalyst activities from those of C$_{60}$/SiO$_2$.

The plot of C_t/C_0 of imidacloprid versus time shows an approximate linearity, and the photoreaction did not fit a first-order kinetic model (Fig. 3). The variation in the rate of decrease for imidacloprid was similar to that of methyl orange. The adsorption of imidacloprid onto the Pe/SiO$_2$ powder would affect the photoreaction.

The mass spectrum of the filtered solution after the irradiation (60 min) is shown in Fig. 4. The product was identified as imidacloprid desnitro from the mass spectrum. The compound is also the photoreaction product of imidacloprid by direct UV irradiation [24]. No peaks assignable to the products were observed by ESI/MS. The formation of NO$_3^-$ was confirmed by ion chromatography. The NO$_3^-$ was quantitatively produced from the consumed imidacloprid. However, the formation of Cl$^-$ ions were not observed. The dechlorinaton from imidacloprid did not occur during the photoreaction.

Based on these facts, it is proposed that the photoreaction of imidacloprid in the presence of Pe/SiO$_2$ and ascorbic acid proceeds through the two possible mechanisms outlined in Fig. 5. The first step is the photoexcitation of Pe/SiO$_2$ for both mechanisms. Thus, the electron transfer from the excited perylene to imidacloprid or $^3O_2$ occurs, and forms the radical anion of imidacloprid or oxygen, respectively. The mechanism via electron transfer from the excited perylene to imidacloprid is similar to that for the decomposition of methyl orange by Pe/SiO$_2$. The radical anion of imidacloprid undergoes bond cleavage to generate imidacloprid desnitro and NO$_3^-$. In the case of the mechanism to form the superoxide anion radical, the formed oxygen radical anion attacks imidacloprid, and causes the cleavage and oxidation of the NO$_2$ group in imidacloprid to produce the NO$_3^-$ ion. Ascorbic acid will give an electron to the radical cation of perylene.

The rate of decrease (%) of imidacloprid slightly decreased by the removal of oxygen (Table 2, entries 6 and 8 or entries 7 and 9). This

Table 2
Photoreaction of imidacloprid using Pe/SiO$_2$ as a photocatalyst.

Entry	Additives	Atmosphere	Light	Irradiation time (min)	Rate of decrease (%)
1	Pe/SiO$_2$	Air	Visible light (>420 nm)	60	5.3
2	Ascorbic acid (AA)	Air	Visible light (>420 nm)	60	0
3	None	Air	Visible light (>420 nm)	60	2
4	Pe/SiO$_2$	Air	Dark	60	10
5	Pe/SiO$_2$ + AA	Air	Dark	60	11
6	Pe/SiO$_2$ + AA	Air	Visible light (>420 nm)	30	60
7	Pe/SiO$_2$ + AA	Air	Visible light (>420 nm)	60	99
8	Pe/SiO$_2$ + AA	N$_2$	Visible light (>420 nm)	30	57
9	Pe/SiO$_2$ + AA	N$_2$	Visible light (>420 nm)	60	92
10	Pe/SiO$_2$ + AA	Air	Sunlight	30	42
11	Pe/SiO$_2$ + AA	Air	Sunlight	60	49

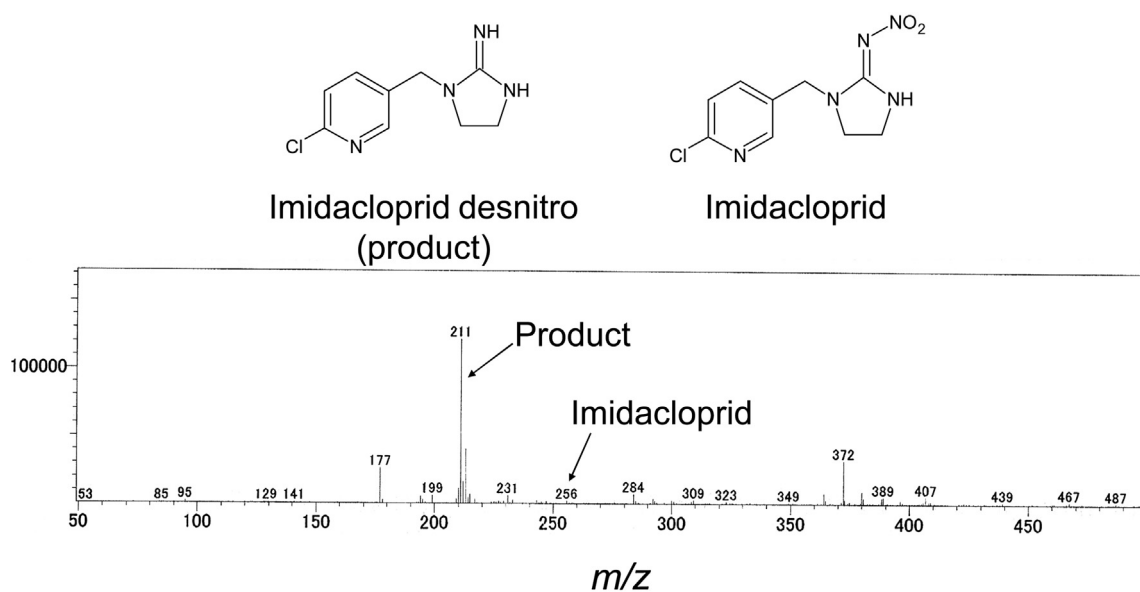Imidacloprid desnitro
(product)

Imidacloprid

Fig. 4. Mass spectrum of the filtered solution after the photoreaction of imidacloprid with Pe/SiO$_2$ in the presence of ascorbic acid for 1 h. The initial concentrations of imidacloprid and ascorbic acid were 50 μM and 5.0 mM, respectively.
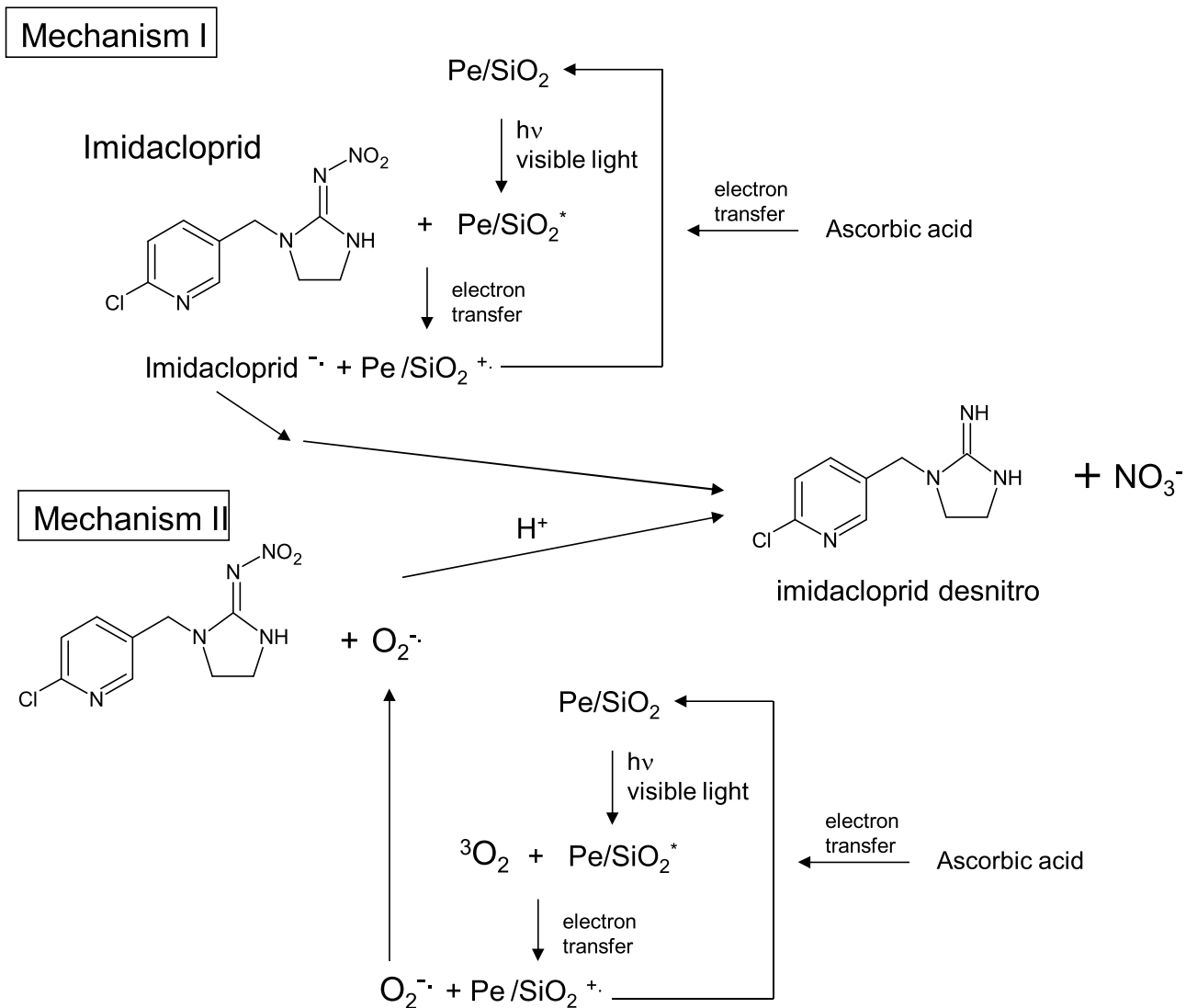

Fig. 5. A possible mechanism for the photoreaction of imidacloprid with Pe/SiO$_2$ in the presence of ascorbic acid.
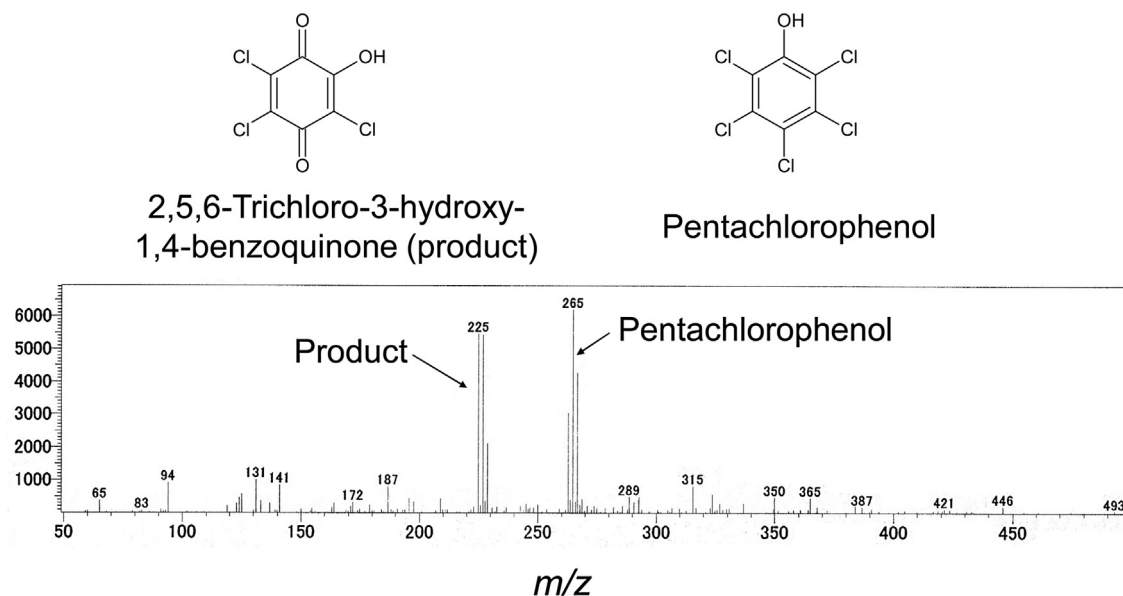
Fig. 6. Mass spectrum of the filtered solution after the photoreaction of PCP with Pe/SiO$_2$ for 2 h. The initial concentration of PCP was 10 μM.

result indicated that formation of the superoxide anion radical by electron transfer between the excited perylene and oxygen slightly affects the decomposition of imidacloprid.

Irradiation by sunlight of the imidacloprid aqueous solution with the Pe/SiO$_2$ powder in the presence of ascorbic acid also resulted in the decomposition of the imidacloprid, and the products were also imidacloprid desnitro and NO$_3^-$.

3.4. Photoreaction of pentachlorophenol (PCP) in the presence of Pe/SiO$_2$ powder

PCP was adsorbed on the glassware in the presence of ascorbic acid (pH 4) due to the equilibrium of the PCP between the neutral and anionic species. Therefore, the photoreaction of PCP with Pe/SiO$_2$ in the presence of ascorbic acid could not be observed. The photoreaction of PCP with Pe/SiO$_2$ in the absence of ascorbic acid (pH 6.2) was then studied. Irradiation of the PCP aqueous solution with the Pe/SiO$_2$ powder in the absence of ascorbic acid resulted in the decomposition of the PCP. The rate of decrease of PCP by the irradiation of visible light for 4 h was 54%. The reaction did not occur in the absence of Pe/SiO$_2$ or in the dark. In addition, PCP was not decomposed by the irradiation of visible light using C$_{60}$/SiO$_2$ as a photocatalyst. The results are summarized in Table 3.

The mass spectrum of the reaction solution after the irradiation (2 h) is shown in Fig. 6. The peaks at m/z 225–231 of the product were observed. The products of the photoreaction were assigned to 2,5,6-trichloro-3-hydroxy-1,4-benzoquinone (TCHB) based on ESI/MS and LC/MS measurements. The retention times of the product in the reaction solution by the LC/MS measurements were in agreement with those of the standard samples of TCHB. In addition, the formation of Cl$^-$ was confirmed by ion chromatography. The yields of TCHB by the irradiation of visible light for 2 h were 96%. The yield of TCHB was calculated based on the consumed PCP.

The plot of C$_t$/C$_0$ of PCP versus time does not show a linearity. In the cases of methyl orange and imidacloprid, a good linearity of the plot was observed (Figs. S4 and 3). On the other hand, the plot of −ln (C$_t$/C$_0$) of PCP versus time shows an approximate linearity (Fig. 7b). This result suggested that the photoreaction fit a first-order kinetic model. The kinetic model of the photoreaction was different from those of methyl orange and imidacloprid. PCP did not significantly adsorb onto the Pe/SiO$_2$ in the absence of ascorbic acid,
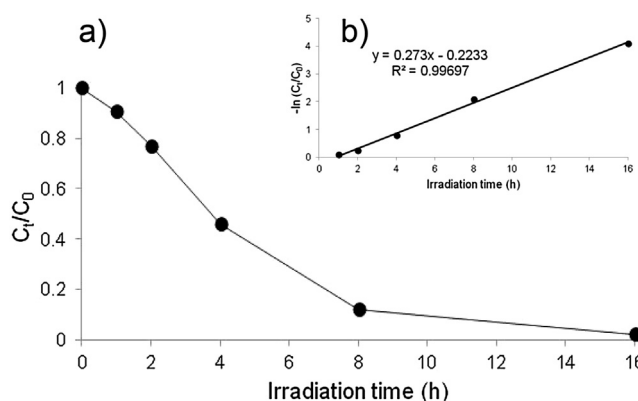

Fig. 7. (a) The changes in the concentration of PCP by the photocatalytic process. (b) Pseudo-first order plots of degradation of PCP vs. irradiation time.

and the adsorption of PCP onto Pe/SiO$_2$ would not affect the kinetics of the photoreaction. Changes in the concentration of TCHB and chloride through the photoreaction of PCP are shown in Fig. 8. The concentration of TCHB decreased by the irradiation of visible light for more than 4 h. On the other hand, the concentration of chloride increased by the irradiation, and the quantity of chloride was more than that calculated based on the formation of TCHB from PCP. This
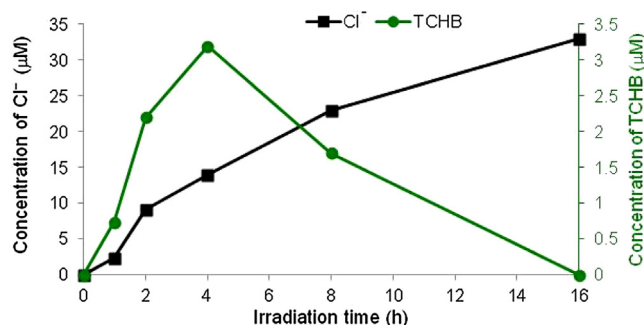

Fig. 8. The changes in the concentration of chloride and TCHB by the photoreaction of PCP with Pe/SiO$_2$.

Table 3
Photoreaction of pentachlorophenol using Pe/SiO$_2$ as a photocatalyst.

Entry	Additives	Light	Irradiation time (h)	Rate of decrease (%)
1	None	Visible light (>420 nm)	2	0.76
2	Pe/SiO$_2$	Dark	2	9
3	Pe/SiO$_2$	Visible light (>420 nm)	1	9.3
4	Pe/SiO$_2$	Visible light (>420 nm)	2	23
5	Pe/SiO$_2$	Visible light (>420 nm)	4	54
6	Pe/SiO$_2$ + 2-propanol[a]	Visible light (>420 nm)	2	30

[a] The concentration of 2-propanol was 0.1 M.

result indicated that TCHB was dechlorinated by the photoreaction. The mass spectrum of the reaction solution after the irradiation for 16 h is shown in Fig. S9. The peak intensity of TCHB decreased compared to the mass spectrum in Fig. 6 (irradiation time: 2 h), and peaks corresponding to other products at m/z 131–133 and m/z 209–213 were detected. The result also indicated that the produced TCHB was converted to other compounds by visible light irradiation in the presence of Pe/SiO$_2$. It was reported that PCP was oxidized to TCHB by hydroxyl radicals produced by the electro-Fenton process. [25] The addition of 2-propanol increased the decomposition (%) of PCP (Table 3, entries 4 and 6).

Based on these facts, it is proposed that the photoreaction of PCP in the presence of Pe/SiO$_2$ proceeds through the possible mechanisms outlined in Fig. 9. The first step is the photoexcitation of Pe/SiO$_2$. Thus, the electron transfer from PCP to the excited perylene forms the radical anion of perylene and the radical cation of PCP. The radical cation of PCP would then be attacked by OH$^-$ to yield the intermediate I in Fig. 9. The next step is a back electron transfer from the radical anion of perylene to the intermediate I producing chloranil. Chloranil undergoes an electron transfer from the excited perylene to generate TCHB. The formation of the superoxide anion would suppress these electron transfer systems.

4. Conclusion

Pe/SiO$_2$ could be used as a novel visible light-sensitized photocatalyst for the decomposition of pollutants. Imidacloprid and pentachlorophenol were not decomposed by the visible light irradiation in the presence of C$_{60}$/SiO$_2$. On the other hand, these compounds were decomposed by the visible light irradiation in the presence of Pe/SiO$_2$. Furthermore, perylene is low-cost compared to C$_{60}$ fullerene. Based on these results, we concluded that peryleneis useful for the material of a visible-light response photocatalyst to decompose environmental pollutants in water.

Perylene is not listed in US EPA carcinogen list, and the compound is considered not classifiable as to its carcinogenicity to human (IARC group 3). However, there is a report about the toxic effects of perylene on the bacterioplankton and the suspended bacteriobenthos [26]. Therefore, it is necessary to develop the system to avoid diffusing perylene in the environment, when the technique apply to real environmental samples.

Furthermore, the use of ascorbic acid for water purification is questionable because of cost-effectivity and the diffusion of ascorbic acid in the environment. We have already confirmed that methyl orange was decomposed by Pe/SiO$_2$ powder using Fe^{2+} as
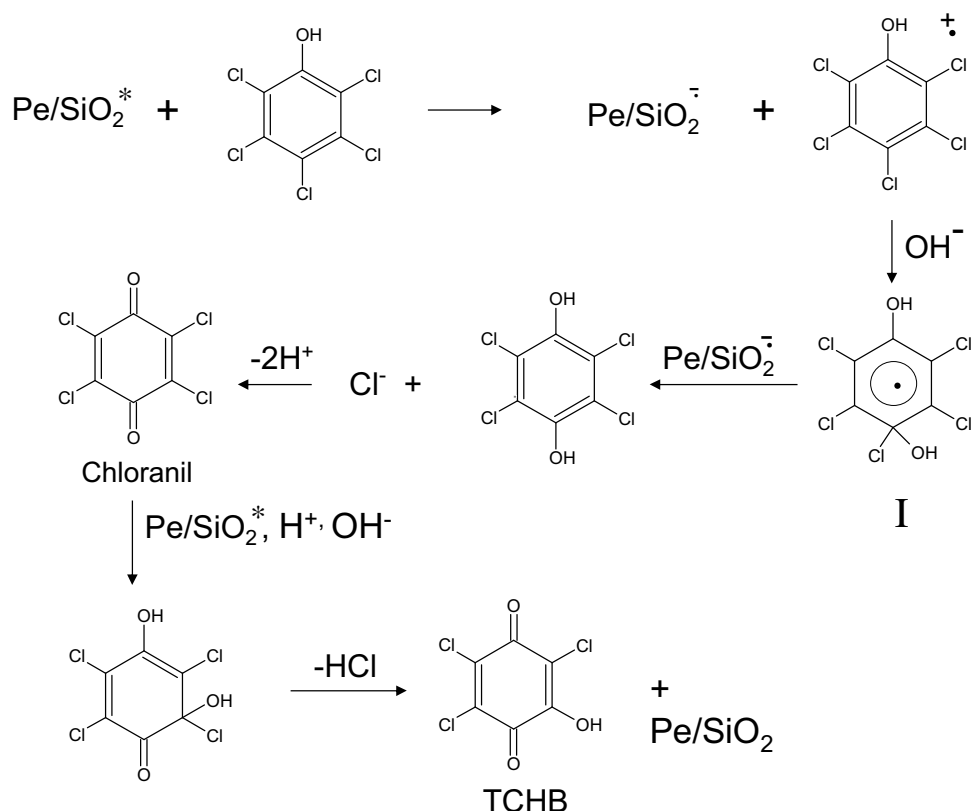
Fig. 9. A possible mechanism for the photoreaction of PCP with Pe/SiO$_2$.

an electron donor instead of ascorbic acid. The decomposition (%) of methyl orange by the visible-light induced reaction system using Fe^{2+} was 47% (irradiation time: 2 h).

In addition, further reactions of the products to minerals by using Pe/SiO_2 as a photocatalyst were not sufficient. Therefore, it is needed to develop a method to mineralize the products of the photoreactions. The dechlorination of pentachlorophenol by the visible light irradiation is a unique photoreactivity of Pe/SiO_2. The dechlorination reaction is a very important process for the decomposition of organochlorine contaminants, such as organic chlorine insecticides, organochlorine pesticides, and polychlorinated biphenyl. It is expected to use the Pe/SiO_2 powder for the decomposition of various organochlorine contaminants.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2016.11.056.

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